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THERMOCHEMISTRY OF GASEOUS COMPOUNDS OF METALS
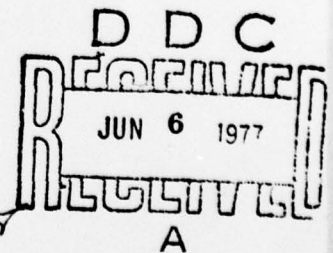
Prepared by

D. L. Hildenbrand

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Prepared for

Air Force Office of Scientific Research (NA)
Building 410
Bolling Air Force Base
Washington, D.C. 20332

Attention: Dr. J. F. Masi

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Thermochemical studies of gaseous IIA monohalides CaBr, SrBr, BaBr, and BaCl were carried out by high temperature mass spectrometry. The monohalides were generated by the reaction of HBr or HCl with appropriate metal oxides in molydbenum effusion cells. Dissociation energies and standard heats of formation were evaluated from various equilibrium measurements at temperatures of 1800 to 2000 K. Preliminary thermochemical data were obtained for gaseous BaI. In the course of the work, the gaseous oxybromide OBBr was also observed, and thermochemical data were derived. From studies of the vaporization of

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$CaBr_2$, $SrBr_2$, and $BaBr_2$ by the torsion-effusion methods, values were derived for the heats of sublimation/vaporization, heats of formation, and dissociation energies of the gaseous dibromides. The derived dissociation energies of the monohalides are compared with values obtained from flame equilibria, chemiluminescence, ionic model calculations, and Birge-Sponer extrapolations; the results provide an interesting comparison of the experimental methods, and give further information about chemical bonding in the monohalides.

ABSTRACT

Thermochemical studies of the gaseous IIA monohalides CaBr, SrBr, BaBr, and BaCl were carried out by high temperature mass spectrometry. The monohalides were generated by the reaction of HBr or HCl with appropriate metal oxides in molybdenum effusion cells. Dissociation energies and standard heats of formation were evaluated from various equilibrium measurements at temperatures of 1800 to 2200 K. Preliminary thermochemical data were obtained for gaseous BaI. In the course of the work, the gaseous oxybromide OBBr was also observed, and thermochemical data were derived. From studies of the vaporization of $CaBr_2$, $SrBr_2$, and $BaBr_2$ by the torsion-effusion method, values were derived for the heats of sublimation/vaporization, heats of formation, and dissociation energies of the gaseous dibromides. The derived dissociation energies of the monohalides are compared with values obtained from flame equilibria, chemiluminescence, ionic model calculations, and Birge-Sponer extrapolations; the results provide an interesting comparison of the experimental methods, and give further information about chemical bonding in the monohalides.

INTRODUCTION

The screening of candidate reactions for efficient electronic-transition chemical lasers requires, initially, an accurate value for the dissociation energy, D_0^0, of the stable molecular product of the exothermic pumping reaction. From D_0^0, the reaction exothermicity and the accessibility of excited electronic states can be evaluated as a first step in the screening process; subsequent information about branching ratios, vibrational populations, radiative lifetimes and related topics is required for detailed analysis of lasing possibilities. Metal-halogen reactions have been among those considered for laser applications, with the alkaline earth (IIA) metals frequently used because of their relatively high volatilities and the expected stabilities of the monohalides. Although the IIA monofluorides and monochlorides have been reasonably well characterized by thermochemical methods, the monobromides and monoiodides have not. Chemiluminescent reaction studies of some IIA monohalides have been reported recently, and they indicate D_0^0(MX) values which are substantially (10-20 kcal/mol) higher than thermochemical or predicted values. New thermochemical measurements on the IIA halides were undertaken as part of this program in order to resolve conflicts with the chemiluminescent reaction studies, and to obtain detailed comparison with several bonding models which can be used to estimate dissociation energies. The results of our studies on calcium, strontium and barium bromides are reported here, along with some new data on gaseous BaCl, BaI and OBBr.

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RESULTS

Isomolecular exchange reactions of CaBr, SrBr, and BaBr with AlBr were studied by mass spectrometry, using the reaction of HBr with the pertinent metal oxides in a molybdenum effusion cell to generate the desired gaseous products. For the Sr-Al-Br work, a small amount of AlB_{12} was added to increase the aluminum activity, leading to the observation and characterization of OBBr. BaCl and BaI were produced when HCl and HI were used as reactive gases. Presence of the IIA mono-halides was indicated by the observation of MX^+ at a threshold appearance potential very close to that of the corresponding metal. $AlCl^+$ and $AlBr^+$ had identical threshold AP's of 9.3 eV, while $OBBr^+$ appeared at 12.5 eV, indicative that each is a parent ion.

The gaseous equilibrium measurements are summarized in Table 1. In each instance the results were checked for attainment of gaseous equilibrium by varying the reactive gas flow and changing the relative abundances of gaseous species in the oven source; derived equilibrium constants proved to be independent of gas flow rate over a wide range, indicating gaseous equilibration. Further strong proof of equilibrium behavior comes from the fact that the BaCl derived equilibrium data agree very closely with those obtained earlier using a $BaCl_2$ + Al beam source.[1] The spectroscopic constants of all pertinent molecules are known with reasonable accuracy, so that the derived results are based entirely on a third law analysis. In the final evaluation, all thermo-dynamic functions and auxiliary heats of formation were taken from the JANAF Thermochemical Tables. Derived data for the monohalides are based on the heats of reaction and the established values for $D_0^0(AlBr)$ and $D_0^0(AlCl)$.

In Table II, the $D_0^0(MX)$ data obtained in this work are compared with the results of other evaluation techniques. Agreement of the results on CaBr, SrBr, BaBr and BaCl with the data obtained from flame equilibria[2,3] by spectrophotometry is remarkably good in all respects, while the chemiluminescence results[4] are uniformly higher by as much as 21 kcal/mol. Values of $D_0^0(MX)$ calculated from Rittner's polarizable ion model, using procedures outlined earlier,[1] are also in excellent agreement with the thermochemical data, showing that the ionic model can be extremely useful as a source of thermochemical data on molecules of sufficient ionicity such as these. A linear Birge-Sponer extrapolation (LBX) gives values of D_0^0 which are clearly too low, as expected, but the application of a correction factor based on ionic character[1] raises these values to reasonable levels. Even so, the corrected LBX values for CaBr, SrBr and BaBr are on the average about 6 kcal/mol higher than the thermochemical data. Uncertainties in the vibrational anharmonic constant could account for part of the discrepancy. On the whole, only the chemiluminescent reaction data of Menzinger[4] are out of line; note that this technique yields lower bounds to D_0^0. It must be concluded from these comparisons that photon yields observed in the chemiluminescent studies under beam-gas conditions are not resulting solely from single collision events, and that multiple collision processes must make a major contribution. These factors must be taken into account in any scaling-up of the laboratory experiments into a lasing device.

In conjunction with another program, the vaporization behavior of $CaBr_2$, $SrBr_2$, and $BaBr_2$ was studied by the torsion-effusion method, using a platinum effusion cell. $CaBr_2$ and $BaBr_2$ were studied in both the solid and liquid ranges. The results were analyzed with auxiliary

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data from the JANAF Thermochemical Tables to give the derived quantities shown in Table III. In general, the results support the molecular constant assignments for the gaseous dibromides; the third law heats are therefore preferred.

The standard heats of formation and dissociation energies derived from this work are summarized in Table IV.

PUBLICATIONS

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Table 1

SUMMARY OF GASEOUS EQUILIBRIUM DATA

Reaction	Data Points	Range, K	$\Delta H_T(II)$ kcal/mol	$\Delta H_{298}(II)$ kcal/mol	$\Delta H_{298}(III)$ kcal/mol
Ca + AlBr = CaBr + Al	6	1972–2158	21.0 ± 4.9	21.0	26.9
Sr + AlBr = SrBr + Al	7	1819–2005	17.5 ± 2.0	17.5	21.6
Ba + AlBr = BaBr ± Al	13	1962–2186	16.4 ± 3.3	16.9	14.9
Ba + AlCl = BaCl + Al	4	2039–2165	-	-	13.5
Ba + BaI$_2$ = 2 BaI	6	1873–2011	-	-	22.9
BO + AlBr = OBBr + Al	7	1819–2005	- 4.6 ± 6.2	- 7.2	0.8

II = second law.
III = third law.

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Table 2

COMPARISON OF D_0^0(MX) VALUES, kcal/mol

	This Work	Flame Equilibria	Chemi-Luminescence	Ionic Model	LBX	LBX(corr)
CaBr	73.4 ± 2	75.7 ± 5.5[b]	97.4 ± 1.5[d]	75	67	80
SrBr	78.7 ± 2	78.4 ± 4.5[b]	93.5 ± 2[d]	78	65	84
BaBr	85.5 ± 2	87.5 ± 2.0[b]	104.6 ± 2[d]	84	64	92
BaCl	105.2 ± 2 105.5 ± 2[a]	106.8 ± 2.0[c]	119.7 ± 1.5[d] 110 ± 3[e]	101	62	105
BaI	71.2 ± 4	-	-	67	57	70

a Reference 1
b Reverence 2
c Reference 3
d Reference 4
e Reference 5

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Table 3

VAPORIZATION DATA FOR DIBROMIDES

	Points	Range,	ΔS_T(II) cal/mol	ΔH_T(II) kcal/mol	ΔH_{298}(II) kcal/mol	ΔH_{298}(III) kcal/mol
$CaBr_2$(s) = $CaBr_2$(g)	17	934-1002	35.3 ± 1.0	65.1 ± 1.0	68.2	71.8
$CaBr_2$(ℓ) = $CaBr_2$(g)	18	1024-1287	29.1 ± 0.6	58.9 ± 0.8	66.4	67.4
$SrBr_2$(ℓ) = $SrBr_2$(g)	19	1080-1251	31.3 ± 0.6	65.9 ± 0.8	74.6	71.5
$BaBr_2$(s) = $BaBr_2$(g)	21	1048-1118	38.4 ± 0.7	74.9 ± 0.8	80.2	79.9
$BaBr_2$(ℓ) = $BaBr_2$(g)	18	1135-1275	32.4 ± 0.7	68.4 ± 0.9	75.8	73.4

(II) = second law.

(III) = third law.

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Table 4

SUMMARY OF DERIVED THERMODYNAMICS DATA

	ΔHf^0_{298} kcal/mol	D^0_{298} kcal/mol
CaBr	- 4.4	74.0
SrBr	-13.3	79.3
BaBr	-16.4	86.0
BaCl	-34.0	105.8
BaI[*]	- 3.6	71.7
OBBr[*]	-73.4	292.5
$CaBr_2$	-91.3	186.6
$SrBr_2$	-97.0	189.7
$BaBr_2$	-101.1	197.4

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*Preliminary values.